

(72) GUILLET, James E., CA

(72) BURKE, Nicholas A.D., CA

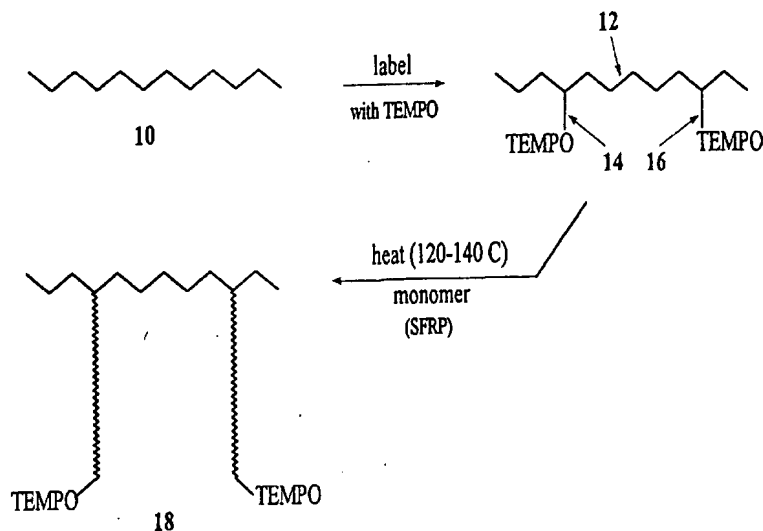
(71) GUILLET, James E., CA

(71) BURKE, Nicholas A.D., CA

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(54) **PROCEDE DE POLYMERISATION AVEC GREFFAGE**

(54) **GRAFT POLYMERIZATION PROCESS**



(57) Graft copolymers having side chains or branches of substantially uniform length and molecular weight are prepared by a process in which the backbone polymer is treated to create carbon centered free radicals thereon, e.g. by radiation, in the presence of a stable free radical compound. The free radical sites bond to the stable free radical through thermally labile bonds, so that heating of the "labelled" polymer in the presence of polymerizable monomer causes re-formation of the carbon centered free radicals with dissociation of the polymer-stable free radical compound bond, to effect graft copolymerization of the monomer. Controlled polymerization takes place by repetition of the three steps (dissociation, monomer addition, re-association) to give a graft copolymer with substantially uniform branch chains, each capped with a stable free radical group.



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ABSTRACT OF THE DISCLOSURE

Graft copolymers having side chains or branches of substantially uniform length and molecular weight are prepared by a process in which the backbone polymer is treated to create carbon centered free radicals thereon, e.g. by radiation, in the presence of a stable free radical compound. The free radical sites bond to the stable free radical through thermally labile bonds, so that heating of the "labelled" polymer in the presence of polymerizable monomer causes re-formation of the carbon centered free radicals with dissociation of the polymer-stable free radical compound bond, to effect graft copolymerization of the monomer. Controlled polymerization takes place by repetition of the three steps (dissociation, monomer addition, re-association) to give a graft copolymer with substantially uniform branch chains, each capped with a stable free radical group.

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CANADA

TO WHOM IT MAY CONCERN:

BE IT KNOWN that we GUILLET, James E., Canadian citizen of 31 Sagebrush Lane, Don Mills, Ontario, Canada, M3A 1X4 and BURKE, Nicholas A.D., Canadian Citizen of 12 Tally Ho Road, Dundas, Ontario, Canada, L9H 3M6, have invented certain new and useful improvements in

GRAFT POLYMERIZATION PROCESS

of which the following is a specification.

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GRAFT POLYMERIZATION PROCESS

FIELD OF THE INVENTION

5 This invention relates to graft copolymers, and more particularly to processes for the preparation of graft copolymers of controlled molecular weight.

BACKGROUND OF THE INVENTION

10 Graft copolymers comprise a backbone polymer having a plurality of polymeric branches attached thereto, at different sites along the backbone polymer. The backbone polymer and the graft polymer may be comprised of one or more monomers, and may be of the same or a different chemical constitution from one another. By using different
15 combinations of monomers for the backbone polymer and the graft polymer, copolymers having interesting combinations of properties can be prepared. High impact polystyrene is an example of a graft copolymer, in which a rubbery polymer such as polybutadiene is used as the backbone polymer and
20 styrene is grafted thereon as branch chains of polystyrene. The presence of the rubbery backbone polymer confers on the resulting high molecular weight product a significantly increased impact strength, as compared with homopolymeric polystyrene, so that the resultant product has a
25 combination of properties derived from the individual constituents.

Graft copolymers are commonly made by free radical initiated, solution, suspension or bulk polymerization.
30 The preformed backbone, is mixed with the grafting monomer or monomers, and subjected to the action of free radicals which cause the development of grafting sites on the

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backbone polymer chains and polymerization of the grafting monomers onto the grafting sites. Such a process is, however, random and uncontrolled, except within very broad ranges. The resulting graft copolymer has a non-homogeneous composition, with graft chains of widely varying molecular weight and length, and including non-grafted homopolymers and copolymers of the grafting monomers. Whilst such a non-homogeneous polymeric product is suitable for many applications, there are instances where a more homogeneous product, of pre-determined molecular weight and having the graft copolymer (branches) thereof of generally consistent length and molecular weight, is desirable.

It is an object of the present invention to provide a graft polymerization process which allows control over the length and molecular weight of the graft polymer branches which are formed.

SUMMARY OF THE INVENTION

The process of the present invention takes advantage of the properties of stable free radicals in effecting graft copolymerization onto a preformed polymeric backbone. In the process, the backbone polymer is caused to react with molecules of a stable free radical, to attach them to the backbone, at locations to act as potential grafting sites. Stable free radicals have the property of existing, in free radical form, in solution at ordinary room temperatures for extended periods of time. They do not react with themselves, or with other oxygen-centered free radicals, to any significant degree, and hence can exist in solution in relatively high concentrations. They will,

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however, readily react with carbon-centered free radicals, for example, with polymer-centered free radicals.

Thus, the creation of free radical sites on the backbone polymer of a potential graft copolymer, in solution or suspension, or on the surface of said polymers, containing stable free radicals, will cause the stable free radicals to attach to the backbone polymer at the free radical sites. These are the potential grafting sites in the formation of the graft copolymer.

The linkage between the backbone polymer and the stable free radical is thermally labile. Accordingly, when the backbone polymer-stable free radical combination is appropriately heated, in solution or suspension containing the graft monomer or monomers, the linkage can undergo a reversible dissociation. Dissociation of the backbone polymer-stable free radical linkage leaves carbon-centered free radicals on the polymer which initiate graft polymerization of the graft monomer or monomers onto these free radical sites, with the free radical becoming dispersed on the growing polymer chain end. The free radical at the distal end of the graft chain will recombine with the stable free radical, in a step which is the reverse of the dissociation step. As heating continues, the stable free radical may be dissociated again, at which time the graft chain may be extended by the incorporation of additional monomer units. Repetition of these three steps (dissociation, addition of monomer, re-association of stable free radical) during heating leads to slow and controlled growth of the side chains. The growth of the graft chains is an example of a stable free radical polymerization (SFRP). By adjustment of the heating time, along with appropriate choice of graft monomer

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concentration, the length and molecular weight of the graft polymer chain can be controlled. Moreover, substantial uniformity between the graft copolymer chains as regards their length and molecular weight can be achieved. The
5 total molecular weight of the graft copolymer will also depend on the number of grafting sites per backbone polymer.

Thus, according to the present invention from one
10 aspect, there is provided a process for preparing graft copolymers having graft chains of controlled molecular weight, which comprises:

preparing a solution or dispersion or solid surface of a preformed backbone polymer;

15 creating free radical sites on the backbone polymer;
chemically attaching stable free radicals to said free radical sites;

effecting controlled graft polymerization at the sites of attachment of said stable free radicals by changing the
20 solution conditions so as to cause dissociation of the stable free radical attachments with formation of free radical sites at the sites of attachment, in the presence of a free radical polymerizable monomer;

effecting free radical graft polymerization of graft
25 monomer onto said free radical sites to form graft polymer chains, with the stable free radical chemically attached to the distal end.

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BRIEF REFERENCE TO THE DRAWINGS

Figure 1 of the accompanying drawings is a diagrammatic representation of the scheme for preparing graft copolymers according to the invention;

Figures 2, 3, 4 and 5 are presentations of the results of GPC analysis of the various products prepared according to Example 1 described herein;

Figures 6 and 7 are GPC chromatograms of products of Example 2 below;

Figures 8 and 9 are GPC chromatograms of products of Example 3 below;

Figure 10 is a GPC chromatogram of the product of Example 4 below.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Suitable backbone polymers for the present invention include substantially any polymer on which carbon-centered free radical sites can be generated. The polymers include hydrocarbon polymers including polyethylene, polypropylene, polystyrene, polybutylene, other polyolefins and the like, and unsaturated hydrocarbon polymers such as polybutadiene, polystyrene, polyisoprene; copolymers of hydrocarbon monomers such as ethylene-propylene copolymers and ethylene-propylene-diene terpolymers (EPDM), polymers of vinyl group monomers containing functional groups such as polyacrylic acid, polymethacrylic acid, polyacrylates, polymethacrylates, copolymers thereof such as poly(ethylene-vinyl acetate), carbohydrate polymers such as

celluloses, starches, nucleic acids and dextran; polyesters; polyamides; polypeptides; and the like. One of the advantages of the present invention lies in the fact that it can be worked with backbone polymers containing normally unreactive functional groups.

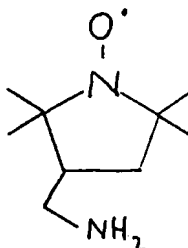
Free radical sites on the backbone polymers can be prepared, according to the process of the present invention, by a variety of different techniques. For example, they can be prepared radio chemically - the passage of gamma rays (from a cobalt-60 source for instance) through a sample will create a number of radical species. They can be prepared photochemically, e.g. by irradiation of a suitable compound (benzophenone, anthraquinone, polymerization photoinitiator) to produce species (radicals, excited states) capable of H-abstraction from the polymer chain. They can be produced chemically, using systems such as Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and polymerization initiators (benzoyl peroxide, AIBN, persulfate) to produce radicals capable of hydrogen abstraction.

The process of the present invention creates the free radical sites on the backbone polymer in solution or at the surface of a solid polymer, and chemically attaches stable free radicals to these free radical sites. Oxygen centered radicals are preferably used as the reactive radicals in the chemical process for producing free radicals on the polymer backbone chain, because stable free radicals react rapidly with carbon-centered radicals but not with most oxygen-centered radicals. Accordingly, radicals derived from compounds such as hydrogen peroxide, benzoyl peroxide and anthraquinone will be oxygen-centered and less likely to react with the stable free radical.

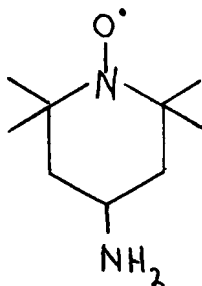
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The stable free radicals useful in the present invention are thus those which can exist in solution for at least 24 hours in free radical form, without recombining with one another to any substantial extent. They are highly reactive with carbon-centered free radicals, but substantially unreactive with oxygen-centered free radicals, and accordingly are derived from oxygen-centered free radical generating compounds themselves. They are known in the art, and representative ones of them are commercially available. The most common type of stable free radicals are aminoxyl radicals (also known as nitroxyl radicals or nitroxides), examples of which include:

3-aminomethyl-PROXYL (AMP) of chemical formula:



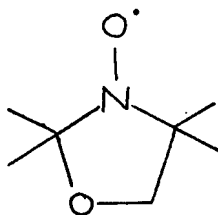
4-amino-TEMPO (AT), of chemical formula:



and

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DOXYL, of chemical formula:



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Graftable comonomers for use in the present invention

10 include substantially any monomer which can be polymerized by free radical mechanisms, in solution or suspension. They include styrene, ethylene, propylene, butylene, butadiene, isoprene, isobutylene, vinyl acetate, acrylic acid, methacrylic acid, methylmethacrylate, vinyl chloride

15 and the like, and combinations of 2 or more such monomers.

The process of the present invention, in its preferred embodiment, proceeds by first attaching to the backbone

20 polymer a stable free radical compound, by subjecting the backbone polymer to free radical creating conditions in the presence of the stable free radical compound. The bond